Arsenic in Natural Phosphates and Phosphate Fertilizers

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INTRODUCTION

Arsenic is widely distributed in nature, though usually in "trace" quantities (*100, pp. 3–13*).[3] According to Clarke and Washington (*22, pp. 20–21*), arsenic occupies the thirty-eighth position in the order of abundance of the elements in the igneous rocks of the world, and its concentration therein, like that of molybdenum, rubidium, tin, and bromine, falls within the range 1×10^{-6} to 9×10^{-6} percent. Not only is arsenic a common constituent of rocks, minerals, coals, soils, sediments, and waters (see table 13), but it is nearly always present in vegetation (*2a, 46, 52, 54, 59, 86, 146*), particularly marine growths (*18, 43, 85, 146*); in the tissues of mammals, fish, and crustaceans (*12, 13, 18, 45, 46, 52, 54, 59*); and in atmospheric dusts, especially those of industrial districts and large cities (*36, 49*).

Inasmuch as crude sulfuric acid manufactured from pyrite and other sulfide ores, especially by the chamber process, usually contains an appreciable quantity of arsenic (*1, 16, 28, 58, 88, 127, 130; 149, pp. 337–338*), products made either directly or indirectly with such acid often contain notable amounts of this element (*1, 15, 16, 39, 40, 44, 57, 76, 88, 108, 109, 127, 147*). The presence of arsenic in superphosphate was pointed out by Davy (*28*) in 1859, and subsequently a few scattered results for this element in fertilizers and

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[3] Italic numbers in parentheses refer to Literature Cited, p. 31.

fertilizer materials have appeared in the literature (*2a, 5, 42, 48, 49, 56, 58, 59, 67, 68, 73, 81, 89, 94, 104, 120, 130, 131, 151*).

Results are given in this publication for arsenic in 210 samples of mineral phosphates from various deposits of the world, 16 samples of calcined, sintered, nodulized, and defluorinated phosphates, 30 samples of commercial superphosphates, 6 samples of crude phosphoric acid produced by the sulfuric acid process, and 19 samples of other phosphatic materials. The results for arsenic in natural phosphates represent an extension of the studies of this Division on the composition of phosphate rock (*60, 61, 64, 65, 66, 68, 69, 80, 81, 82, 97, 98, 110, 111, 118*).

METHOD OF ANALYSIS

The method used for the determination of arsenic is substantially the one developed by Deemer and Schricker (*30*) for the analysis of plant materials, with the inclusion of certain improvements suggested by Schricker and Dawson (*123*). The method comprises the digestion of the sample with a mixture of sulfuric and nitric acids, the distillation of the arsenic as the trichloride, essentially by Taber's procedure (*133*), and its determination by the molybdenum-blue colorimetric method proposed by Denigès (*31, 32*). Denigès' original procedure has been modified and improved by Truog and Meyer (*138*) and Zinzadze (*152, 153*), as well as by Schricker and coworkers (*30, 123*).

The authors' application of the method to the determination of arsenic in phosphates can be conveniently presented under the subjects: (1) Reagents and glassware, (2) separation of arsenic from the sample, and (3) procedure used.

REAGENTS AND GLASSWARE

On account of the relatively large quantity of reagents required for the determination of the small quantities of arsenic involved (usually less than 50 parts per million), special attention had to be given to the arsenic content of the reagents. Sodium carbonate, beta-dinitrophenol, molybdenum trioxide, and molybdenum metal are used in such small quantities that they are not likely to introduce significant amounts of arsenic. Hydrochloric, nitric, and sulfuric acids, ammonium oxalate, and potassium bromide of reagent grade, and sodium chloride that had been purified for biological work were very satisfactory. Cuprous chloride that meets the American Chemical Society's specifications for analytical reagent chemicals (*10*) is not suitable because of the relatively high arsenic tolerance (50 p.p.m.). Cuprous chloride that contains not more than 0.5 p. p. m. of arsenic can, however, be obtained from certain manufacturers of laboratory chemicals.

In 1935, Lockemann (*92, 93*) pointed out that hot, concentrated sulfuric acid dissolves appreciable quantities of arsenic from Jena glass, and he expressed the opinion that disregard of this factor has caused serious error in many of the older determinations of arsenic. Deckert (*29*) said the quantity of arsenic dissolved from the glass during the analysis can be greatly decreased by first boiling concentrated sulfuric acid in the flask for at least 2 hours; also, he stated

that arsenic-free Jena glass is manufactured. Pyrex chemical glass-ware made prior to about the middle of the year 1934 contained a few tenths of 1 percent of arsenic, but analyses of the glass manufactured since that time show less than 0.3 p. p. m. of arsenic (*134, 143*).[4]

Confirming Deckert's results (*29*), the reagent blank obtained with previously used flasks was practically the same for high-arsenic glass as for low-arsenic glass (table 1). It will be noted that the reagent blank was significantly higher with new flasks of low-arsenic glass that had not been used previously. In the presence of fluorine-bearing materials, however, the quantity of arsenic obtained with flasks made of high-arsenic glass was 1.6 to 9.2 times that found with flasks of low-arsenic glass. As phosphate rock usually contains 3 to 4 percent of fluorine (*81, 82, 98, 118*) and this element is also an important con-stituent of superphosphates (*63, 82*), as well as of certain other phos-phatic fertilizers,[5] such materials should be digested in glassware that contains little or no arsenic. Likewise, Rader and Hill (*111*) found that the use of boron-containing glassware causes large errors in the determination of boron in phosphate rock, superphosphate, and other fluorine-bearing materials. Furthermore, the use of bottles for the storage of superphosphates and other materials that contain active fluorine compounds may also result in serious contamination of the sample with arsenic from the glass (p. 25).

TABLE 1.—*Derivation of arsenic from glassware in the analysis of fluorine-bearing materials*

Material analyzed	Arsenic found by digestion in—	
	Low-arsenic glass [1]	High-arsenic glass [1]
	Milligrams	*Milligrams*
Reagents alone	[2] 0. 0078	
Do	. 0050	0. 0048
Reagents+0.1 gm. fluorspar	. 0104	. 0832
Reagents+0.1 gm. sodium fluoride	. 0096	. 0888
Reagents+1 gm. phosphate rock [3]	. 0188	. 0299

[1] 500-ml. Kjeldahl flasks of Pyrex glass.
[2] New flasks, not previously used; all other digestions were made in flasks that had been used a number of times.
[3] Florida land pebble, standard sample No. 120 of the National Bureau of Standards, contained 3.76 percent of fluorine (*73*).

By careful selection of the chemicals and the use of low-arsenic glassware, the reagent blanks were kept below 0.006 mg. of arsenic throughout this investigation.

SEPARATION OF ARSENIC FROM THE SAMPLE

The authors' recovery of arsenic from monopotassium arsenate, alone and in the presence of phosphate rock, is shown in table 2. The results are in good agreement with those reported by Deemer and Schricker (*30*).

[4] Also, SHETTERLY, F. F. Private communication. Corning Glass Works, Corning, N. Y.
[5] For example, the materials listed in table 17 as Nos. 1885, 1849, 1901, 1902, 1021, 1588, and 1172 contain 3.38, 2.63, 2.41, 1.25, 3.96, 0.83, and 2.06 percent of fluorine, respectively.

TABLE 2.—*Recovery of arsenic from monopotassium arsenate by digestion and distillation*

Material or mixture	Arsenic from monopotassium arsenate		
	Present	Recovered	
	Milligrams	*Milligrams*	*Percent*
Monopotassium arsenate (KH₂AsO₄)	0.005	0.0050	100.0
	.005	.0050	100.0
	.025	.0255	102.0
	.025	.0248	99.2
	.100	[1].1017	101.7
	.100	[1].1006	100.6
KH₂AsO₄+1 gm. phosphate rock [2]	.025	.0246	98.4
	.025	.0247	98.8

[1] Distillate was made up to a volume of 100 ml., and 25-ml. aliquots were used for development of the molybdenum-blue color.
[2] Florida land pebble, standard sample No. 120 of the National Bureau of Standards.

Experiments by Hoffman and Lundell (*74*) indicate that boron, germanium, mercury, rhenium, antimony, selenium, and tin, if present in the digested sample, may follow the arsenic, completely or in part, into the distillate. Extensive determinations of these elements in mineral phosphates have been made only in the case of selenium (*110*) and boron (*111*). Small quantities of selenium, such as those present in soils and phosphate rocks, do not interfere in the determination of arsenic by the molybdenum-blue method (*126*). Little or no interference by boron is indicated by the small effect of fluoride additions on determinations made in low-arsenic glass, in comparison with the effect of such additions on those made in high-arsenic glass (table 1), although considerable boron is doubtless dissolved from both kinds of glass in the presence of fluorine.

Small quantities of tin have been reported in double superphosphate and bonemeal (*42*) and in phosphate rocks from Florida, Tennessee, and Maxville, Mont. (*42, 73, 106*). Hill, Marshall, and Jacob state that samples of Florida land pebble, Tennessee blue rock, and Idaho phosphates were tested for molybdenum with negative results (*68*). However, neither of these elements would be expected to interfere in the determination of arsenic. Spectrochemical analyses by Seribner (*73*) showed no antimony in one sample each of Florida land pebble and Tennessee brown rock; so far as the authors know, these are the only tests that have been made for antimony in natural phosphates. According to Byers and Robinson,[6] small quantities of antimony do not interfere in the determination of arsenic by distillation with hydrobromic acid at 126° C. and subsequent analysis of the distillate by the molybdenum-blue method.

Apparently no tests for rhenium in natural phosphates have been made, and, so far as the authors know, only two samples of phosphate rock have been examined for mercury, both with negative results (*73*). Likewise, spectrochemical analyses showed no germanium in Florida land pebble, Tennessee brown rock, and Maxville, Mont., phosphates (*73, 106*). The authors' experiments indicated little or no interference by added germanium in the determination of arsenic.

Silica interferes slightly when the quantity in the final solution exceeds 1 mg. per milliliter (*123*). In the analysis of fluorine-bearing materials, silica may be present in the solution as a result of volatiliza-

[6] BYERS, H. G., and ROBINSON, W. O.   Private communication.   Bureau of Plant Industry.

tion in combination with fluorine during the distillation. That such volatilization occurs only to a negligible extent, if at all, is indicated by the fact that distillates from 1-gm. samples of phosphate rock (3.56 percent fluorine) contained no more than 0.1 mg. of fluorine. Furthermore, there was no evidence of interference by the fluorine itself.

Phosphorus interferes quantitatively in the molybdenum-blue test for arsenic (*123*). Hoffman and Lundell (*74*) found that some phosphorus is volatilized when phosphates are heated at 200° to 220° C. with mixtures of hydrochloric or hydrobromic and sulfuric or perchloric acids in a moderate stream of dry carbon dioxide, and Reynolds (*116*) reported the presence of phosphorus in certain distillates obtained by heating phosphates with perchloric acid at temperatures not higher than 150°. In the determination of arsenic, the maximum temperature in the distillation mixture is approximately 125°, and the presence of phosphorus in the distillate has not been observed.

Total arsenic, as distinguished from acid-soluble arsenic obtained by direct digestion of the sample, was determined in a few typical phosphate rocks by fusing the sample with 2.2 times its weight of a mixture of sodium carbonate (1 part) and sodium nitrate (0.1 part) prior to the acid digestion (*70, p. 209*). The results showed little or no increase in the recovered arsenic as a result of fusion of the sample.

PROCEDURE USED

Add 10 ml. of concentrated nitric acid and 30 ml. of concentrated sulfuric acid to the sample, preferably of such weight that the arsenic content is 0.005 to 0.040 mg.,[7] in a 500-ml. Kjeldahl flask of arsenic-free glass. (Concentrated sulfuric acid should be boiled in new flasks for at least 1 hour before they are placed in use.) Heat the flask until strong fuming sets in, boil the contents for 30 minutes, and then cool to room temperature. Add 20 ml. of distilled water, and mix the contents of the flask by gentle swirling, add 2 gm. of ammonium oxalate, rinse the walls of the flask with 2 to 3 ml. of water, and boil the contents for 30 minutes. Cool the flask, and dilute the contents with 25 ml. of water; if nitrous fumes are evolved add more ammonium oxalate, and repeat the digestion.

Add to the cold digestion mixture 30 gm. of sodium chloride, 2 gm. of cuprous chloride, 0.5 gm. of potassium bromide, and 25 ml. of concentrated hydrochloric acid, and immediately close the flask with a rubber stopper carrying a Hopkins trap fused to a delivery tube (3 mm. inside diameter, constricted to about 1 mm. inside diameter at the exit). Allow the delivery tube to extend within 2 to 3 mm. of the bottom of a 100-ml. graduated cylinder that contains 70 ml. of distilled water and is immersed in an ice bath. Heat the Kjeldahl flask and control the rate of distillation so that 25 ml. of distillate are obtained in about 30 minutes. A resistance unit of the type used in electrically heated Kjeldahl outfits is a very convenient source of heat for the distillation.

After the distillation is completed, add 10 ml. of concentrated nitric acid to the solution in the graduated cylinder, transfer the contents to a 150-ml. beaker, and evaporate on a steam bath or hot plate to a

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[7] Although larger samples can be used, the quantity of arsenic in the solution at the time the molybdenum-blue color is developed should fall within these limits.

volume of approximately 10 ml. with the occasional addition of 1 to 2 ml. of concentrated nitric acid, if necessary, to insure complete elimination of chlorine from the solution. Evaporate the colorless solution to dryness on a steam bath, add 1 to 2 ml. of concentrated nitric acid, and again evaporate to dryness. Finally, add 1 ml. of a 1-percent solution of sulfuric acid and evaporate on the steam bath to the consistency of a thick sirup.

Dissolve the sirupy solution in 7 to 10 ml. of hot water, and transfer it to a 50-ml. volumetric flask, taking care that the total volume of the solution is slightly below 40 ml. Add 1 drop of a saturated aqueous solution of beta-dinitrophenol, make slightly alkaline with a 0.36 N aqueous solution of sodium carbonate, and carefully neutralize with 1-percent sulfuric acid solution. Then add exactly 0.5 ml. of molybdenum-blue reagent,[8] rinse the neck of the flask with a small quantity of distilled water, adjust the volume of the solution to approximately 40 ml., and heat the flask on a steam bath for 1 hour with occasional swirling of the contents. Cool the solution, dilute it with distilled water to a volume of 50 ml., and immediately compare the color with that of similarly treated standard arsenic solutions by means of either a visual or a photoelectric colorimeter. As pointed out by Deemer and Schricker (*30*), further dilution of the solution after the volume has been adjusted to 50 ml. is not permissible.

A photoelectric colorimeter[9] is preferable to a visual instrument. Its use not only affords greater precision but also eliminates the personal equation from the matching of the colors and the necessity for the continual preparation of fresh standards. According to Schricker and Dawson (*123*), the precision of the molybdenum-blue method is approximately 0.001 mg. of arsenic in 50 ml. of solution when the color intensity is measured with a photoelectric colorimeter.

With samples of phosphates containing up to 100 p. p. m. of arsenic, the difference between duplicate determinations seldom exceeded 0.5 p. p. m. and was usually less than 0.3 p. p. m. of arsenic. With larger quantities of arsenic the differences were frequently somewhat greater.

ARSENIC IN MINERAL PHOSPHATES

Results for acid-soluble arsenic in mineral phosphates are given in tables 3, 4, 5, 6, and 7 and are summarized in table 8. Values for phosphorus pentoxide content are also given in these and later tables for purposes of comparison. Except as otherwise indicated, the analytical data in these and other tables are reported on the moisture-free basis (105° C.). For individual samples of all types and sources of phosphate, the results range from 0.4 p. p. m. in a Florida soft phosphate (No. 1091, table 3) to 188.2 p. p. m. in an Arkansas phosphate (No. 1712, table 5). The arsenic contents of the South Carolina river rock (average 68.4 p. p. m.), Arkansas phosphate (average 61.0

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[8] Heat a quantity of molybdenum trioxide in an electric muffle furnace at approximately 500° C. for 1 hour, and dissolve 48 gm. of the cold, ignited trioxide in 1 liter of hot, concentrated sulfuric acid, stirring frequently (solution 1). Dissolve 4.8 gm. of the ignited trioxide and 0.7 gm. of pure molybdenum metal powder in 100 ml. of hot, concentrated sulfuric acid, stirring frequently (solution 2). Cool the solutions, and prepare the reagent solution by diluting 100 ml. of solution 2 to 1 liter with solution 1.

[9] Practically all of the results for arsenic given in this publication were obtained with the aid of a photoelectric colorimeter that was copied, with slight modification, from an instrument constructed by John A. Schricker of this Bureau (private communication). The general principle of the colorimeter is similar to that of the instruments described by Zinzadze (*154*) and Barton and Yoe (*9*).

p. p. m.), and Montana phosphate (average 47.6 p. p. m.) are, in general, considerably higher than those of the other phosphates. At the other extreme are Florida hard rock and Virginia apatite, with averages of 5.4 and 5.5 p. p. m., respectively. Florida land pebble and Tennessee brown rock, the most widely used of the domestic phosphates, average 11.9 and 14.6 p. p. m. of arsenic, respectively.

TABLE 3.—*Arsenic in Florida phosphates*

LAND-PEBBLE PHOSPHATE

Sample No.	Location of deposit	P_2O_5	As	Sample No.	Location of deposit	P_2O_5	As
		Percent	*P. p. m.*			*Percent*	*P. p. m*
[1] 1448	Bartow	28. 23	18. 5	627	Lakeland	33. 70	13. 4
1853	do	30. 37	10. 5	1891	Not known	33. 80	8. 5
618	Pierce	30. 53	18. 2	1873	do	34. 03	12. 1
[2] 617	Brewster	30. 70	19. 7	1884	do	34. 12	15. 4
619	Nichols	30. 98	11. 6	1855	do	34. 41	7. 6
910	Mulberry	31. 09	[3] 21. 2	[4] 1310	Mulberry	34. 44	14. 2
947	Brewster	31. 28	17. 3	1851	Bartow	34. 88	8. 4
790	Not known	31. 40	12. 3	[5] 1447	do	35. 11	11. 4
1879	do	32. 32	16. 3	[4] 1445	Pembroke	35. 16	8. 3
1857	do	32. 35	15. 4	[4] 1302	Mulberry	35. 18	18. 3
1893	do	32. 82	8. 8	912	do	35. 37	[3] 10. 6
1895	do	33. 02	12. 5	1859	Not known	35. 38	3. 6
[5] 439	Mulberry	33. 22	9. 8	[6] 120	Mulberry	35. 40	12. 9
1882	Not known	33. 47	8. 3	1867	Not known	35. 47	4. 3
622	Nichols	33. 56	5. 4	898	Lakeland	35. 55	5. 5
1875	Bartow	33. 59	9. 9				

HARD-ROCK PHOSPHATE

771	Not known	31. 25	[3] 3. 0	434	Dunnellon	35. 33	1. 4
[2] 590	Benotis	33. 52	6. 8	[2] 588	Floral City	35. 70	2. 8
[2] 591	Inverness	33. 52	8. 7	[2] 623	Hernando	35. 74	4. 6
[2] 589	Floral City	34. 68	7. 1	932	Dunnellon	35. 99	[3] 9. 1

SOFT PHOSPHATE

1091	Bartow	25. 47	0. 4	728	Juliette	31. 80	[2] 5. 9
[7] 580	Not known	29. 49	18. 6	1450	Rital	32. 78	5. 5
[8] 1359	Hardee County [9]	30. 32	13. 3	443	Gilchrist County	34. 94	1. 3

WASTE-POND PHOSPHATE

581	Not known	18. 18	7. 1	915	Dunnellon	23. 63	[3] 5. 3
828	Felicia	19. 83	9. 5	1459	Felicia	25. 11	12. 1
727	Dunnellon	21. 63	9. 2	725	Juliette	25. 31	8. 0
726	Felicia	23. 48	10. 4	1455	Hernando	32. 30	10. 4

RIVER-PEBBLE PHOSPHATE

[10] 1846	Liverpool [11]	27. 77	21. 2				

[1] Dust recovered from exit gases of dryers and kilns.
[2] Sample representative of large shipment.
[3] Analysis reported by Jacob, Hill, Marshall, and Reynolds (*81, p. 30*).
[4] Concentrated by froth flotation.
[5] Concentrated by oiling and tabling.
[6] Standard sample number of the National Bureau of Standards. Hoffman and Lundell (*75*) reported 13.6 p. p. m. of As in this sample.
[7] Contains much aluminum phosphate.
[8] Contains principally aluminum phosphate.
[9] Deposit east of Peace River, near Wauchula.
[10] Commercial material as formerly produced.
[11] De Soto County.

TABLE 4.—*Arsenic in Tennessee phosphates*

BROWN-ROCK PHOSPHATE

Sample No.	Location of deposit	P₂O₅	As	Sample No.	Location of deposit	P₂O₅	As
		Percent	*P. p. m.*			*Percent*	*P. p. m.*
[1] 1321	Franklin	19.46	9.2	762	Mount Pleasant	33.73	7.9
[2] 1922	Columbia	22.85	56.1	906	Wales	34.39	[3] 24.2
[1] 1918	Franklin	22.95	7.4	1861	Not known	34.40	6.6
1916	Mount Pleasant	28.38	7.6	908	Mount Pleasant	34.44	13.0
1482	Match	28.67	12.3	1863	Not known	34.52	11.9
587	Wales	30.17	25.9	1871	do	34.53	5.1
[4] 56	Not known	31.28	28.9	1899	do	34.84	6.6
1346	Centerville	32.07	22.6	1869	Wales	34.92	13.1
1926	Mount Pleasant	32.08	13.4	1897	do	34.96	7.7
564	Wales	32.85	17.9	1342	Mount Pleasant	35.77	10.5
[4] 56a	Mount Pleasant	32.94	14.2	[5] 1317	Not known	36.52	14.8
1924	do	33.53	7.2	[5] 1401	Wales	36.74	13.8
1889	Siglo		6.4				

BLUE-ROCK PHOSPHATE

Sample No.	Location of deposit	P₂O₅	As	Sample No.	Location of deposit	P₂O₅	As
[6] 571	Gordonsburg	27.90	16.6	[6] 576	Gordonsburg	31.22	21.4
[6] 572	do	29.16	19.8	448	do	32.03	21.4
772	Glover	30.45	[3] 17.4	449	do	33.65	8.4
930	Gordonsburg	30.97	37.7				

WHITE-ROCK PHOSPHATE

Sample No.	Location of deposit	P₂O₅	As	Sample No.	Location of deposit	P₂O₅	As
1483	Perry County	28.41	21.7	1031	Godwin	35.80	4.8
1048	Tomscreek	30.20	5.2				

PHOSPHATIC LIMESTONE

Sample No.	Location of deposit	P₂O₅	As	Sample No.	Location of deposit	P₂O₅	As
446	Gordonsburg	10.16	13.9	447	Mount Pleasant	14.04	11.4
916	Mount Pleasant	11.22	6.9	770	Not known	19.13	23.5
917	Gordonsburg	11.68	17.3				

OTHER PHOSPHATES

Sample No.	Location of deposit	P₂O₅	As	Sample No.	Location of deposit	P₂O₅	As
1516	Mountain City [7]	29.26	8.6	[8] 1049	Boma [9]	31.22	8.9

[1] Matrix.
[2] Mixture of matrix and washed phosphate sand; used for production of sinter for electric furnace smelting.
[3] Analysis reported by Jacob, Hill, Marshall, and Reynolds (*81*, p. *30*).
[4] Standard sample number of the National Bureau of Standards. Hoffman and Lundell (*73*) reported 15.9 p. p. m. of As in this sample.
[5] Concentrated by froth flotation.
[6] Sample representative of large shipment.
[7] Johnson County.
[8] Kidney phosphate.
[9] Putnam County.

TABLE 5.— *Arsenic in Arkansas, Kentucky, Oklahoma, South Carolina, and Virginia phosphates*

ARKANSAS PHOSPHATES

Sample No.	Location of deposit	P_2O_5	As	Sample No.	Location of deposit	P_2O_5	As
		Percent	*P. p. m.*			*Percent*	*P. p. m.*
[1] 1703	Independence County.[2]	21. 14	67. 3	[1] 1713	Independence County [2]	29. 02	60. 6
[1] 1710	do [3]	22. 34	44. 9	[1] 1707	do [3]	31. 51	42. 8
[1] 1712	do [3]	23. 96	188. 2	[3] 1267	do [3]	31. 98	32. 6
[1] 1705	do [3]	27. 14	36. 7	[1] 1708	do [3]	33. 73	14. 6

KENTUCKY PHOSPHATES

Sample No.	Location of deposit	P_2O_5	As	Sample No.	Location of deposit	P_2O_5	As
[4] 1235	Wallace	21. 19	10. 3	[4] 1234	Wallace	27. 80	6. 7
[5] 1245	do	23. 68	12. 7				

OKLAHOMA PHOSPHATES

Sample No.	Location of deposit	P_2O_5	As	Sample No.	Location of deposit	P_2O_5	As
[1] 1714	Pontotoc County	12. 60	17. 9	[1] 1716	Craig County	27. 51	19. 3
[3] 1242	Cotton County	24. 31	15. 6				

SOUTH CAROLINA LAND-ROCK PHOSPHATE

Sample No.	Location of deposit	P_2O_5	As	Sample No.	Location of deposit	P_2O_5	As
[6] 495	Not known	16. 07	9. 2	[7] 1137	Charleston [8]	27. 58	18. 9
[7] 1139	Johns Island [9]	26. 92	27. 5	[7] 1138	do [8]	27. 85	[10] 12. 9

SOUTH CAROLINA RIVER-ROCK PHOSPHATE

Sample No.	Location of deposit	P_2O_5	As	Sample No.	Location of deposit	P_2O_5	As
[1] 1646	Broad River [11]	20. 74	88. 1	1647	Broad River	26. 97	67. 9
[1] 1645	Coosaw River [12]	23. 94	60. 7	[1] 1642	Coosaw River [13]	27. 34	56. 8

VIRGINIA PHOSPHATES [14]

Sample No.	Location of deposit	P_2O_5	As	Sample No.	Location of deposit	P_2O_5	As
1136	Piney River	38. 12	6. 6	1295	Piney River	39. 50	4. 3

[1] Prospect sample.
[2] Lafferty Creek area.
[3] Selected material.
[4] Sample from an abandoned mine.
[5] Ground material formerly sold for direct application to the soil.
[6] Museum sample.
[7] Commercial material as formerly produced.
[8] Lamb's mine.
[9] Bulow mines.
[10] Analysis reported by Jacob, Hill, Marshall, and Reynolds (*81, p. 30*).
[11] Mouth of Whale Branch.
[12] Brickyard Point.
[13] Mouth of Bull River.
[14] Fluorapatite concentrate obtained from ilmenite-apatite ore by a magnetic separation process (*58*).

TABLE 6.—*Arsenic in Idaho, Montana, Utah, and Wyoming phosphates*

IDAHO PHOSPHATES

Sample No.	Location of deposit	P_2O_5	As
		Percent	*P. p. m.*
[1] 1607	Bingham County, Wolverine Creek Canyon	22.19	4.5
1411	Bear Lake County, Georgetown Canyon	30.30	8.7
[2] 550	Bear Lake County, Paris area	32.21	21.5
[3] 1609	Caribou County, Wells Canyon	32.21	10.3
[4] 454	Caribou County, Conda	32.24	15.4
[5] 1408	____do	32.26	14.8
[4] 1253	____do	32.36	15.1
[4] 973	____do	32.53	17.7
[4] 1865	____do	32.54	9.8
1608	Caribou County, Diamond Gulch	33.12	10.5
[6] 1617	Bear Lake County, Hot Springs	34.85	7.8
1616	Bear Lake County, Bloomington Canyon	35.15	11.3
1412	Bear Lake County, Slight Canyon	35.39	9.3
1613	Caribou County, Upper Deer Creek Canyon	35.53	25.7
[3] 1614	Caribou County, sec. 9, T. 7 S., R. 44 E	35.95	4.9
1606	Fort Hall Indian Reservation, SE¼ sec. 2, T. 4 S., R. 37 E	36.10	15.0

MONTANA PHOSPHATES

1280	Maxville	24.96	12.3
[7] 1011	Garrison, William Anderson mine	27.63	[8] 66.6
[7] 1009	____do	31.39	[8] 106.0
[4] 1930	____do	31.62	58.7
[7] 1017	____do	34.92	39.7
[4] 1633	Avon, Cronin and Crowley mine	34.97	68.2
[4] 1252	Garrison, William Anderson mine	36.38	41.0
[7] 1010	____do	37.47	[5] 18.2
1407	Avon, Cronin and Crowley mine	37.94	17.7

UTAH PHOSPHATES

[7] 1641	Uintah County, Brush Creek area	16.74	15.3
[7] 1634	____do	20.82	16.4
[7] 1637	____do	26.41	13.2
1490	Morgan County, Weber Canyon	26.80	19.2
[1] 1631	Uintah County, Ashley Creek Gorge	27.62	43.2
1409	Cache County, Logan Canyon	31.50	18.0
1630	Rich County, Brazer Canyon	35.17	8.4
[9] 1629	Rich County, north end of Crawford Mountains	37.87	8.6

WYOMING PHOSPHATES

[1] 1624	Hot Springs County, Bighorn River Canyon	17.56	7.6
[10] 1621	Fremont County, Willow Creek	24.12	10.8
[11] 469	Cokeville, mine of Cokeville Phosphate Co	26.60	18.8
[1] 1623	Fremont County, Little Popo Agie Canyon	27.50	10.9
[12] 1622	Fremont County, Willow Creek	29.06	13.8
948	Cokeville, mine of Cokeville Phosphate Co	30.19	11.7
1625	Lincoln County, Beckwith Hills	31.80	8.0
1626	Lincoln County, Raymond Canyon	33.98	9.8
1627	Teton County, Talbot Creek	37.06	17.3

[1] Sample from outcrop of deposit.
[2] Commercial material as formerly produced.
[3] Float phosphate.
[4] Commercial material.
[5] Composite sample of shipments during the period Sept. 25, 1934, to Jan. 1, 1935.
[6] Partially weathered material from old mine dump.
[7] Prospect sample.
[8] Analysis reported by Jacob, Hill, Marshall, and Rader (*81, p. 30*).
[9] Sample from dump of old Bradley mine.
[10] Sample from outcrop of upper phosphate bed.
[11] Sample representative of large shipment.
[12] Sample from outcrop of lower phosphate bed.

TABLE 7.—*Arsenic in foreign phosphates*

AFRICAN PHOSPHATES

Sample No.	Location of deposit	P_2O_5	As
		Percent	*P. p. m.*
560	Algeria, Dyr	23.39	16.3
1556	Algeria, Djebel Onk	27.05	14.4
1559	Algeria, Djebel Kouif	29.99	7.0
559	Algeria, Bordj-Redir	32.34	36.7
1547	Egypt, Safaga	27.70	22.1
1549	do	32.79	14.1
1571	Morocco, Louis-Gentil	31.86	7.7
1572	Morocco, Kourigha	34.07	9.7
563	Morocco	34.30	16.4
1162	do	35.11	25.2
556	Tunisia, Kalaa-Djerda	26.91	19.1
552	Tunisia, Gafsa	27.55	27.6
1551	do	29.04	9.6

EUROPEAN PHOSPHATES

1462	Austria, Prambachkirchen	27.03	15.3
1226	Belgium, Liege	18.13	54.8
1155	Estonia, Tallinn	25.68	23.9
1240	France, Somme	24.66	22.0
1463	Poland	17.51	19.5
1263	U. S. S. R., Saratov	18.40	15.4
1264	U. S. S. R., Egoriev	22.37	42.0
1262	U. S. S. R., Vyatka	27.88	43.2
[1] 1305	U. S. S. R., Kola Peninsula	31.65	7.6
[2] 1260	do	39.08	7.6

INSULAR PHOSPHATES

1223	Angaur Island, Palau group	40.00	7.4
1297	Assumption Island, Seyehelles group	30.40	17.3
1489	Astove Island, Seychelles group	34.36	21.4
1595	Christmas Island, Indian Ocean	39.35	8.7
452	do	39.46	8.0
1545	Curaçao Island, Netherlands West Indies	30.31	12.0
985	do	38.59	11.8
943	do	40.66	7.6
[3] 1599	Daito Islands, Pacific Ocean	25.62	76.2
1296	Denis Island, Seychelles group	32.88	14.5
[4] 904	Grand Connetable Island, coast of French Guiana	54.51	30.5
1222	Juan de Nova Island, Mozambique Channel	32.29	15.1
1230	Makatea Island, French Oceania	37.94	10.1
1159	do	38.22	7.8
450	Nauru Island, Pacific Ocean	38.92	5.6
1567	do	39.25	5.1
1566	Ocean Island, Gilbert group	40.16	7.9
451	do	40.32	9.7
1597	Peleliu Island, Palau group	37.56	12.0
1591	Rasa Island, Pacific Ocean	30.03	12.7
1306	Walpole Island, New Caledonia group	24.28	40.4

OTHER PHOSPHATES

582	Canada, British Columbia, Crow's Nest Pass	24.11	28.3
[5] 905	Canada, Quebec Province	40.30	28.2
1157	South Australia, Kapunda	30.18	24.3
1158	South Australia, Port Clinton	33.53	20.3

[1] Fluorapatite, crude lumps.
[2] Fluorapatite, concentrated by froth flotation.
[3] Aluminum iron phosphate.
[4] Aluminum phosphate.
[5] Fluorapatite.

TABLE 8.—*Summary of results for arsenic in mineral phosphates*

DOMESTIC PHOSPHATES

Type or source of phosphate	Samples analyzed	Arsenic	
		Range	Average
	Number	*P. p. m.*	*P. p. m.*
Florida land pebble	31	3. 6– 21. 2	11. 9
Florida river pebble	1		21. 2
Florida hard rock	8	1. 4– 9. 1	5. 4
Florida soft	6	. 4– 18. 6	7. 5
Florida waste pond	8	5. 3– 12. 1	9. 0
South Carolina land rock	4	9. 2– 27. 5	17. 1
South Carolina river rock	4	56. 8– 88. 1	68. 4
Fluorapatite from Virginia	2	4. 3– 6. 6	5. 5
Tennessee brown rock	25	5. 1– 56. 1	14. 6
Tennessee blue rock	7	8. 4– 37. 7	20. 4
Tennessee white rock	3	4. 8– 21. 7	10. 6
Tennessee phosphatic limestone	5	6. 9– 23. 5	14. 6
Other Tennessee phosphates [1]	2	8. 6– 8. 9	8. 8
Kentucky	3	6. 7– 12. 7	9. 9
Arkansas	8	14. 6–188. 2	61. 0
Oklahoma	3	15. 6– 19. 3	17. 6
Idaho	16	4. 5– 25. 7	12. 6
Montana	9	12. 3–106. 0	47. 6
Utah	8	8. 4– 43. 2	17. 8
Wyoming	9	7. 6– 18. 8	12. 1

FOREIGN PHOSPHATES

Africa	13	7. 0–36. 7	17. 4
Canada	[2] 2	28. 2–28. 3	28. 3
Europe	[3] 10	7. 6–54. 8	25. 1
Islands	[4] 21	5. 1–76. 2	16. 3
South Australia	2	20. 3–24. 3	22. 3

[1] Kidney phosphate from Boma and phosphate rock from Mountain City.
[2] Including a sample of fluorapatite from Quebec Province.
[3] Including 2 samples of fluorapatite from Union of Soviet Socialist Republics.
[4] Including a sample of aluminum phosphate from Grand Connetable Island and a sample of aluminum iron phosphate from Daito Islands.

Aside from the results on 18 samples of domestic phosphate rocks previously reported from this Division (*68, 81*), very few figures for arsenic in mineral phosphates appear in the literature. Thus, the arsenic content of 9 samples of Florida phosphate rock, presumably land pebble, analyzed by Longfield-Smith (*94*) ranged from a trace to 29 p. p. m., which is in good agreement with the range of results for Florida land pebble given in table 3. Likewise, the figures shown in tables 3 and 4 for the National Bureau of Standards standard samples No. 120 (Florida land pebble) and 56a (Tennessee brown rock), respectively, agree closely with the results reported thereon by Hoffman and Lundell (*73*). Mansfield (*96, p. 212*) states that no arsenic was found in a sample of phosphate rock from Driggs, Idaho, or in a composite sample representing 12 individual samples of high-grade phosphate rock from different parts of the Idaho field. As reported by Williams (*145*), Fairchild found 13 p. p. m. of arsenic in a sample of low-grade phosphatic shale from a prospect hole just north of the mouth of Seymour Canyon, Summit County, Utah, and a sample of oolitic phosphate from an outcrop on the edge of Provo Valley, due north of Midway, Wasatch County, contained less than 6.5 p. p. m. of arsenic.

The spectrochemical results (65 to 326 p. p. m.) of Goldschmidt and Peters (*49*) for arsenic in Angaur Island phosphate are very much higher than the authors' figure (7.4 p. p. m.) on such material (table 7). Also the spectrochemical results (300 and 1,000 p. p. m. of arsenic)

of Noddack and Noddack (*104*) on specimens of fluorapatite from St. Gotthard and Zinnwald, respectively, and those (up to 2,200 p. p. m.) of Haberlandt (*56*) on fluorapatite from Jumilla, Spain, are far higher than the authors' results (4.3 to 28.2 p. p. m.) on fluorapatite from Quebec (table 7), Virginia (table 5), and the Union of Soviet Socialist Republics (table 7). On the other hand, the chemical results (0.6 to 2.3 p. p. m., average 1.6 p. p. m. of arsenic) of Gileva and Melentiev (*48*) on 11 samples of fluorapatite from various localities in the Kola Peninsula, Union of Soviet Socialist Republics, are lower than the authors' figure (7.6 p. p. m.) on 2 samples from this region (table 7).

Arsenic-Bearing Constituents

The data in tables 3 to 7 reveal no uniform relationship between arsenic and phosphoric oxide in the different types and sources of phosphate. In some instances the trend is toward a decrease in arsenic with increasing phosphoric oxide (Algeria, Curaçao Island, Florida soft and land pebble, Montana (Garrison), South Carolina, and Tennessee white rock). In others, the trend seems to be toward an increase in arsenic with increasing phosphoric oxide (Morocco, Tennessee blue rock, and Union of Soviet Socialist Republics), whereas in others there is no trend in either direction. Indications of the probable associations of arsenic with the other constituents of phosphate rock can be obtained from the available data on soils, minerals, etc.

Williams and Whetstone (*146*) recently reported analyses of numerous samples of soils from localities throughout the United States, which, so far as known, had never been artificially contaminated with arsenic. The results showed no uniformity of distribution of arsenic in the soil profile, no observable relation between climatic conditions and arsenic content of soil groups, and no clearly defined, systematic relation between arsenic content and the geological formations from which the soils were developed. In general, however, sandy soils and humid-area soils having high silica-sesquioxide ratios were relatively low in arsenic, whereas soils of subhumid and arid regions tended to be higher in arsenic.

In a study of 20 samples of Italian soils taken from different depths in different geological formations, Zuccàri (*155*) found that soils high in arsenic were also high in iron. Likewise, the investigation by Grimmett and coworkers of the arsenical muds, soils, and waters of the Waiotapu Valley, New Zealand, indicates a definite association of arsenic with iron in this area (*52, 53*). Goldschmidt and Peters (*49*) point out that freshly precipitated ferric hydroxide removes arsenic from aqueous solutions by adsorption. They express the opinion that the arsenic in clayey sediments is likely present as the result of its adsorption by the hydrated ferric oxide in such sediments, and they present evidence to show that the arsenic is associated with the hydrated ferric oxide, as well as with the iron sulfide, in sedimentary rocks. Also, adsorption of arsenious acid by hydrous aluminum oxide has been demonstrated by Yoe (*150*).

The association of arsenic with sulfur in sulfide ores, especially the iron sulfides, has long been known and has been the subject of numerous investigations. Dunn and Bloxam (*36*) attribute the arsenic (50 to 400 p. p. m.) in the atmospheric dusts of English industrial cities

to its presence in the pyrite that occurs in the coal burned in these cities. In this connection, Abel's report *(2a)* of 424.1 p. p. m. of arsenic in a sample of ground coal brasses (pyrite separated from coal) from an unstated course is of interest. On the other hand, Goldschmidt and Peters *(49)* conclude that the arsenic in coal was derived primarily from the vegetable matter from which the coal originated. The widespread occurrence of arsenic in vegetation *(2a, 46, 52, 54, 59, 86, 146)*, especially marine growths *(18, 43, 85, 146)*, lends support to this conclusion. Small quantities of arsenic are commonly present in animal tissues *(12, 13, 18, 45, 46, 52, 54, 59)*, and marine crustaceans and mollusks are exceptionally high in this element. In a study of the slimes of certain lagoons and their tributaries on the Baltic coast of Germany, Goy and Rudolph *(50)* found the arsenic content parallels the content of organic matter; they believe that bacteria are active in removing arsenic from the water and concentrating it in the slime.

In view of the foregoing, some relationship may be expected to exist between the arsenic content of phosphate rock and the quantities of iron, sulfide sulfur, organic carbon, or nitrogen present. The available data (table 9), however, do not point to a regular connection between the arsenic content and any of these constituents. Also, other data (not shown in table 9) indicate no relation between the arsenic and either the aluminum or the total R_2O_3. On the other hand, results for arsenic in the mechanical separates of a Wyoming pyritiferous, highly carbonaceous phosphate rock (table 10), as well as those for arsenic in the separates of an Idaho pyrite-free, highly carbonaceous rock, follow, in general, the results for total iron and organic carbon but not pyrite; arsenic, like the iron and organic carbon, shows marked accumulation in the "clay" fraction. Although the results indicate a better correlation of arsenic with total iron than with organic carbon, they do not permit one to decide whether the arsenic is associated with the iron or organic matter or both. The results on the Florida landpebble (No. 947) and Tennessee brown-rock (No. 908) phosphates, both of which are low in organic carbon (0.29 and 0.11 percent, respectively) and are free from or very low in pyrite, show no correlation between arsenic and total iron in the mechanical fractions. In all the samples, the results indicate considerable loss of arsenic occasioned by suspension of the material in water incident to mechanical separation into fractions.

TABLE 9.—*Comparative results for arsenic, organic carbon, nitrogen, pyritic sulfur, and iron in phosphate rock*

Sample No.	Type or source of phosphate	Organic carbon [1]	As	N	FeS$_2$	Fe$_2$O$_3$ [2]
		Percent	P. p. m.	P. p. m.	Percent	Percent
1280	Montana, Maxville [3]	3.84	12.3	[4]	2.87	[4]
1009	Montana, Garrison [5]	.14	106.0	80	.015	2.11
1010	___do [5]	.09	18.2	80	.015	.56
1252	___do [5]	.09	41.0	[4]	.0	3.10
948	Wyoming, Cokeville [3]	3.47	11.7	1,100	.97	.87
1253	Idaho, Conda	2.86	15.1	[4]	[4]	1.64
973	___do [6]	2.35	17.7	1,000	.0	.87
454	___do [6]	2.29	15.4	910	.0	.80
1412	Idaho, Slight Canyon [5]	.38	9.3	[4]	[4]	[4]
550	Idaho, Paris Canyon [5]	.02	21.5	[4]	.0	.97
1049	Tennessee kidney phosphate	1.46	8.9	2,600	1.51	1.79
552	Tunisia, Gafsa	.86	27.6	470	.0	.65

See footnotes at end of table.

TABLE 9.—*Comparative results for arsenic, organic carbon, nitrogen, pyritic sulfur, and iron in phosphate rock*—Continued

Sample No.	Type or source of phosphate	Organic carbon [1]	As	N	FeS$_2$	Fe$_2$O$_3$
		Percent	*P.p.m.*	*P.p.m.*	*Percent*	*Percent*
771	Florida hard rock	0.52	3.0	180	(4)	1.83
932	do	.18	9.1	50	0.0	.69
1138	South Carolina land rock	.51	12.9	510	.34	1.49
1139	do	(4)	27.5	(4)	.36	1.56
915	Florida waste pond	.47	5.3	440	(4)	4.25
726	do	.22	10.4	240	(4)	3.91
912	Florida land pebble	.38	10.6	130	(4)	.70
910	do	.33	21.2	60	(4)	2.59
619	do	.33	11.6	180	(4)	1.63
947	do	.29	17.3	80	(4)	1.69
439	do	.25	9.8	(4)	(4)	1.90
617	do	(4)	19.7	(4)	.015	2.14
790	do	(4)	12.3	(4)	.0	1.62
772	Tennessee blue rock	.36	17.4	340	2.03	3.54
930	do	.20	37.7	210	3.90	3.42
448	do	(4)	21.4	(4)	1.03	3.30
449	do	(4)	8.4	(4)	2.39	2.35
762	Tennessee brown rock	.29	7.9	150	.0	2.25
7 56	do	.25	28.9	230	.89	3.30
908	do	.11	13.0	40	.0	2.52
906	do	.09	24.2	60	.0	3.42
8 904	Grand Connetable Island	.28	30.5	490	.0	4.43
1031	Tennessee white rock	.36	4.8	330	(4)	.92
1048	do	.09	5.2	160	(4)	1.75
1162	Morocco	.17	25.2	180	.0	.12
985	Curaçao Island	.17	11.8	130	.0	.61
728	Florida soft	.16	5.9	180	(4)	1.54
916	Tennessee phosphatic limestone	(4)	6.9	(4)	.73	1.27
917	do	(4)	17.3	(4)	1.89	1.95

[1] Including also elemental carbon.
[2] Total iron.
[3] Dark-colored pyritiferous rock.
[4] Not determined.
[5] Light-colored rock.
[6] Dark-colored pyrite-free rock.
[7] Standard sample number of the National Bureau of Standards.
[8] Aluminum phosphate.

TABLE 10.—*Distribution of arsenic among mechanical separates of ground phosphate rocks*

Designation	Particle size	Wyoming phosphate No. 948 — Fraction of original material	P$_2$O$_5$	As	Organic carbon [2]	FeS$_2$	FeO$_3$ [3]	Idaho phosphate No. 973 — Fraction of original material	P$_2$O$_4$	As	Organic carbon [2]	FeO$_3$ [3]
	Microns	*Percent*	*Percent*	*P.p.m.*	*Percent*	*Percent*	*Percent*	*Percent*	*Percent*	*P.p.m.*	*Percent*	*Percent*
"Sand"	147 to 50	49.8	33.41	6.5	2.96	0.62	0.46	26.0	35.69	6.6	2.22	0.16
"Silt"	50 to 5	43.6	26.73	7.5	4.25	1.17	1.11	45.5	32.96	8.2	2.03	.40
"Clay"	<5	6.6	23.67	19.8	8.29	.42	2.22	27.9	28.60	32.8	3.03	2.04
Solution and mechanical losses		.0		4 3.9				.6		4 3.1		
Original material		100.0	30.19	11.7	3.47	.97	.87	100.0	32.53	17.7	2.34	.87

Designation	Particle size	Florida land-pebble phosphate No. 947 — Fraction of original material	P$_2$O$_5$	As	Organic carbon	FeS$_2$	FeO$_3$	Tennessee brown-rock phosphate No. 908 — Fraction of original material	P$_2$O$_4$	As	Organic carbon	FeO$_3$
		Percent	*Percent*	*P.p.m.*	*Percent*	*Percent*	*Percent*	*Percent*	*Percent*	*P.p.m.*	*Percent*	*Percent*
"Sand"	147 to 50	48.2	30.97	16.2			1.57	37.6	34.49	10.7		2.16
"Silt"	50 to 5	42.0	31.93	14.1			1.68	46.8	34.85	7.7		2.36
"Clay"	<5	9.6	31.98	14.6			2.34	13.8	32.35	11.4		3.67
Solution and mechanical losses		.2		4 2.2				1.7		4 3.8		
Original material		100.0	31.28	17.3			1.69	100.0	34.44	13.0		2.52

[1] The mechanical fractions were prepared by Alexander and Jacob (5) from material ground to pass a 100-mesh (147μ) sieve.
[2] Including also elemental carbon.
[3] Total iron.
[4] Calculated; based on the original material.

PRIMARY AND SECONDARY DEPOSITS

Following Blackwelder's division (*14*) of the world's phosphate deposits into six genetic varieties, comprised in two broad groups (primary and secondary deposits), Mansfield (*96, p. 362*) has partially classified a number of the deposits.   Accordingly, as far as possible the results for arsenic in phosphate are summarized under the two general groups in table 11.   Although this grouping of the phosphates reveals no definite relationship between arsenic content and the type of the deposit, there is evidence that phosphates from primary deposits tend, in general, to contain somewhat more arsenic than do those from secondary deposits.

TABLE 11.—*Arsenic content of phosphate rocks from primary and secondary deposits*

Type of deposits and location	Samples analyzed	Arsenic	
		Range	Average [1]
Primary:	*Number*	*P. p. m.*	*P. p. m.*
Arkansas	8	14. 6–188. 2	61. 0
Tennessee blue rock	7	8. 4– 37. 7	20. 4
Algeria, Tunisia, and Egypt	9	7. 0– 36. 7	18. 6
Idaho, Montana, Utah, Wyoming, and British Columbia	43	4. 5–106. 0	16. 4
Fluorapatite from Canada, Virginia, and U. S. S. R	5	4. 3– 28. 2	13. 8
Average			26. 0
Secondary:			
South Carolina river rock	4	56. 8– 88. 1	68. 4
South Australia	2	20. 3– 24. 3	22. 3
Islands [2]	21	5. 1– 76. 2	19. 6
South Carolina land rock	4	9. 2– 27. 5	17. 1
Tennessee and Kentucky (brown rock and white rock [3])	32	4. 8– 56. 1	11. 5
Florida	54	. 4– 21. 2	11. 0
Average			25. 0

[1] Average of mean results for individual types or sources of phosphate.
[2] Including aluminum phosphate for Grand Connetable Island and aluminum iron phosphate from Daito Islands.
[3] Including phosphate rock from Johnson County, Tenn.

GEOLOGIC AGE AND ARSENIC CONTENT

In table 12 the results for arsenic in mineral phosphates are grouped, as far as possible, according to the geologic age of the deposits (*77, 139, 145*).   The average figures range from 7.3 p. p. m. in phosphates of Oligocene age (Florida hard rock, soft, and waste pond) to 47.8 p. p. m. in those of Miocene age (South Carolina land rock and river rock), whereas the averages for phosphates of all other periods and epochs are within the limits 11.9 and 24.8 p. p. m.

TABLE 12.—*Geologic age as correlated with arsenic content of natural phosphates*

Period or epoch	Type or source of phosphate	Samples analyzed	Arsenic	
			Range	Average [1]
		Number	*P. p. m.*	*P. p. m.*
Post-Tertiary	Island phosphates and Florida river pebble.[2]	22	5. 1– 76. 2	19. 7
Tertiary	Florida land pebble, hard rock, soft and waste pond; South Carolina, Tennessee white rock,[3] Morocco, and South Australia.	71	.4– 88. 1	18. 5
Pliocene	Florida land pebble	31	3. 6– 21. 2	11. 9
Miocene	South Carolina land rock and river rock	8	9. 2– 88. 1	47. 8
Oligocene	Florida hard rock, soft, and waste pond	22	.4– 18. 6	7. 3
Eocene	Morocco	4	7. 7– 25. 2	14. 7
Cretaceous (or Jurassic)	France, U. S. S. R.,[4] Algeria, Tunisia, and Egypt.	13	7. 0– 43. 2	23. 0
Carhoniferous	British Columbia, Idaho, Montana, Utah, and Wyoming; and Tennessee kidney phosphate.	44	4. 5–106. 0	16. 2
Permian	British Columbia, Idaho, Montana, Utah, and Wyoming.	41	4. 5–106. 0	16. 3
Mississippian	Tennessee kidney phosphate and Utah [5]	3	8. 9– 19. 2	15. 4
Devonian	Tennessee hlue rock	7	8. 4– 37. 7	20. 4
Ordovician	Tennessee and Kentucky hrown rock, Tennessee phosphatic limestone, Arkansas, and Estonia.	42	5. 1–188. 2	24. 8
Pre-Cambrian	Fluorapatite from Virginia and Canada	3	4. 3– 28. 3	16. 9

[1] Average of mean results for individual types or sources of phosphate.
[2] Including aluminum phosphate from Grand Connetahle Island and aluminum iron phosphate from Daito Islands.
[3] Including phosphate rock from Johnson County.
[4] Egoriev, Saratov, and Vyatka.
[5] Logan and Weher Canyons.

PHOSPHATES COMPARED WITH OTHER ROCKS, MINERALS, COALS, SOILS, SEDIMENTS, AND WATERS

Results for arsenic in rocks, minerals, coals, soils, sediments, and waters of the world, collected from various sources, are summarized in table 13. On the basis of these data, it can be concluded that the arsenic content of phosphate rocks is about the same as that of marls, shales (western United States), carbonate minerals, coals, and silicate rocks and minerals. Usually the quantity of arsenic in phosphate rock is greater than that in soils, clays, sediments, and nitrate and halide minerals but is much smaller than that in oxide minerals, greensand, glauconite, and especially sulfide minerals.

TABLE 13.—*Arsenic in rocks, minerals, cools, soils, sediments, ond waters*

Material and location	Literature reference	Samples analyzed	Arsenic	
			Range	Average
		Number	*P. p. m.*	*P. p. m.*
Phosphate rocks; world deposits	(1)	205	0. 4–188. 2	20. 9
Fluorapatite; Virginia, Canada, and U. S. S. R	(2)	5	4. 3–28. 2	13. 8
Igneous rocks:				
Earth's crust	(22, pp. 20–21)			[3] 1–9
America	(21)	[4] 329		4. 8
Meteorites:				
Silicate phase	(103)	42		[5] 20
Iron phase	(103)	16		[5] 360
Trollite phase	(103)	5		[5] 1, 020
Silicate rocks and minerals; 52 species	(104)	265	[5] 0–150	30
Marls; Colorado and Kansas	(59)	4	2. 5–10. 0	5. 1

See footnotes at end of table.

TABLE 13.—*Arsenic in rocks, minerals, coals, soils, sediments, and waters*—Con.

Material and location	Literature reference	Samples analyzed	Arsenic Range	Arsenic Average
		Number	*P. p. m.*	*P. p. m.*
Greensand, glauconite, and glauconite-rich sea sediments.	(49)		[5] 65–325	
Shales:				
Colorado, Kansas, and Montana	(146)	6	2–42	12
Bohemia and Middle Silesia	(72)	11	65–4,824	693
Bauxite	(49)	7	[5] 0–325	
Oxidized iron ores	(49)	19	[5][6] 65–650	
Oxides; 13 species	(104)	47	[5] 5–400	96
Carbonates; 9 species	(104)	13	[5][7] 0–60	17
Nitrates and halides; 7 species	(104)	15	[5] 0–10	3
Sodium chloride; various grades of sea salt and rock salt.	(44)	9	[8]. 025–1.75	.32
Salts of acids of Ti, P, V, Cb, Ta, S, Cr, Mo, and W; 19 species.	(104)	82	[5][9] 0–300	71
Sulfides, selenides, and tellurides; 19 species [10]	(104)	144	[5][11] 10–600	146
Galena; Europe	(71)	19	70–15,80	2,202
Sphalerite; Saxony and Silesia	(71)	11	295–34,630	6,129
Chalcopyrite; Silesia	(71)	3	255–3,825	1,933
Pyrite; Europe, Algeria, and United States	(20, 35, 41, 71, 127; 148, pp. 76–95).	98	0–20,00	5,650
Native sulfur; Europe, Japan, and United States	(2a, 27, 47, 108)	[12] 11	[13] 0–200	43
Native metals; 7 species [10]	(104)	46	[5][14] 0–300	54
Coals; Europe, New South Wales, New Zealand, and United States.	(19, 35, 42, 62, 84, 91, 105).	61	0–200	45
Clays and loams	(104)	52	[5] 0–30	6
Soils:[15]				
Argentina	(115)	20	Trace–22.5	4.4
Costa Rica	(146)	6	.3–5.0	2.3
Italy	(155)	20	1.9–60.0	21.3
Mexico	(146)	18	2.0–40.0	14.3
New Zealand, Waiotapu Valley [16]	(52, 53)	65	8–19,000	
Puerto Rico	(146)	6	.3–4.0	1.5
United States	(59, 86, 95, 146)	233	.2–38.0	7.1
Sediments and sea-bottom material:				
Ocean sediments	(49, p. 12)	57		4
Red clays; oceanic depths	(21)	[4] 51		6.5
Terrigenous clays; oceanic depths	(21)	[4] 52		Trace
Muds; lagoons and their tributaries, Baltic coast, Germany.	(50)	15	1.6–22.7	6.7
Silts; delta of Mississippi River	(21)	[4] 235		2.6
Waters:				
Atlantic Ocean and Baltic Sea	(44, 50, 112)	161	.0008–.08	.015
Vicinity of San Juan Islands, Washington State.	(135, p. 115)		<.03–.03	
Thames and Medway estuaries	(18)	16	.106–.757	.25
Lagoons and their tributaries, Baltic coast, Germany.	(50)	12	Trace–.008	.0024
Salt and mineral springs, France	(44)	6	.01–.31	.18
Hot springs, Yellowstone National Park	(4)	17	0–2.83	1.29
Streams, surface depressions, and hot and cold springs in Waiotapu Valley, New Zealand.	(52, 53)	39	Trace–33.71	3.14
Underground sources in Argentina	(7, 8, 114)	22	0–1.40	.18
English rivers	(18)	2		Trace

[1] Results from tables 3 to 7, exclusive of fluorapatite.
[2] Results from tables 5 and 7. I. Noddack and W. Noddack reported more than 1,000 p. p. m. of arsenic in fluorapatite from Zinnwald and 300 p. p. m. in fluorapatite from St. Gotthard, as determined by a spectrochemical method (104). By means of a similar method, Haberlandt found up to 2,200 p. p. m. of arsenic in apatite from Jumilla, Spain (56). Gileva and Melentiev reported 0.6 to 2.3 p. p. m. of arsenic (average 1.6 p. p. m.) in 11 samples of fluorapatite from various localities in the Kola Peninsula, U. S. S. R., as determined by a chemical method (48).
[3] The average arsenic content is estimated to be within these limits.
[4] A composite sample was analyzed.
[5] Analyses by spectrochemical method.
[6] No arsenic was found in several specimens of micaceous iron shales and a hematite with jasper.
[7] A specimen of cerussite contained more than 1,000 p. p. m. of arsenic.
[8] The sample that contained 1.75 p. p. m. of arsenic was from a fissure in Vesuvius Volcano.
[9] Specimens of descloizite, monazite, pyromorphite, and vanadinite and a fluorapatite from Zinnwald contained more than 1,000 p. p. m. of arsenic.
[10] Including only those species of which the commonly accepted formulas do not show arsenic.
[11] Specimens of argyrodite, galena, tetrahedrite, franckeite, stibnite, copper selenide, sulvanite, zincblende, and stannite contained more than 1,000 p. p. m. of arsenic.
[12] Including the sample referred to in table 16, footnote 3.
[13] Phipson reported 11.16 percent arsenic in sulfur from the solfatara of Naples (107).
[14] Specimens of lead and bismuth contained more than 1,000 p. p. m. of arsenic.
[15] So far as known, these soils had never been artificially contaminated with arsenical compounds.
[16] Including samples of muds.

ARSENIC IN CALCINED, SINTERED, NODULIZED, AND DEFLUORINATED PHOSPHATE ROCKS

For a number of years it has been the practice of several domestic producers to heat a portion of their output of phosphate rock at temperatures (about 815° to 1,370° C.) considerably higher than are necessary merely to remove the bulk of the moisture (11, 90, 101). Thus, more or less complete destruction of the organic matter and elimination of carbon dioxide and combined water are effected, and part of the fluorine may be volatilized, with the result that the grade of the rock is raised, and a product, commonly called calcined phosphate,[10] more suitable for the manufacture of phosphate chemicals by acid-decomposition processes is obtained. For use in the manufacture of phosphoric acid by the sulfuric acid process, phosphate rock from the Conda, Idaho, deposit must be heated to eliminate most of the organic matter, which otherwise would seriously foul the acid and apparatus (90). Although coal is used to some extent, oil is commonly used in this calcining process.

In 1918, Waggaman and Wagner (142) showed experimentally that mine-run phosphate rock can be smelted in the electric furnace. Later experiments (141) showed that such material can also be smelted in fuel-fired furnaces, and several years ago the suitability of sintered Florida land-pebble phosphate matrix [11] as a raw material for the blast-furnace production of phosphorus was demonstrated (117). Sintered Tennessee brown-rock matrix, as well as nodulized matrix and phosphate sand, is now being used in the electric-furnace production of phosphorus and phosphoric acid (26, 87, 139). Coal and oil are used as fuels in the preparation of the nodulized products, whereas the sintered material is prepared with coke. The maximal temperatures range from about 900° to 1,450° C.

Removal of fluorine from phosphate rock can be effected by heating the rock at 1,400° C. or higher temperatures in the presence of silica and water vapor (25, 83, 99, 119). When it is properly prepared this defluorinated phosphate [12] is almost completely soluble in neutral ammonium citrate solution, and it is an excellent source of phosphorus for the growth of plants on neutral and acid soils (79, 121).

As coal usually contains notable quantities of arsenic (table 13), the presence of this element in coke is to be expected. Thus, several investigators (6, 19, 91, 105, 125, 128, 137) have reported arsenic in 29 samples of coke (principally English), ranging in quantity from 2 to 243 p. p. m. and averaging 59 p. p. m. Also, the spectrochemical results of Goldschmidt and Peters (49) showed 65 to 650 p. p. m. of arsenic in the ash of numerous samples of brown coal and anthracite. Determinations of the so-called volatile and fixed arsenic indicate that considerably more than 50 percent of the arsenic in coal and coke usually remains in the ash when these fuels are burned under ordinary conditions (19, 62, 91, 105, 128, 137). It appears, therefore, that the

[10] The term "calcined phosphate" has also been applied to the citrate-soluble products obtained either by heating phosphate rock with alkali salts (55) or by heating it in the presence of silica and water vapor (119). For the purpose of this bulletin, however, the term will be restricted to phosphate rock that has been heated primarily for the purpose of increasing its grade and its suitability for treatment by acid-decomposition processes.
[11] The term "matrix," as used in this bulletin, refers to the natural mixture of phosphate rock and gangue.
[12] The term "defluorinated phosphate" comprises the material known as calcined phosphate that is prepared by defluorinating phosphate rock at temperatures below the melting point (83, 99, 119, footnote 10), as well as the material known as fused phosphate rock which is prepared by defluorinating the molten rock (85).

direct heating of phosphate rock with coal or coke may lead to contamination of the product with arsenic from the fuel. Although data on the arsenic content of fuel oil are not available, Shirey (*124*) reports that a careful spectrochemical examination revealed no arsenic in a sample of ash specially prepared from the still-coke of Kansas crude petroleum.

The arsenic in 16 samples of calcined, nodulized, sintered, and defluorinated phosphates ranged from <1 to 150 percent of that in the parent rocks and was with few exceptions notably lower in the products than in the parent materials (table 14). In general, the arsenic content of the products does not appear to be related either to the arsenic content of the parent materials, the type of fuel used, or to the time or temperature of heating. The data (see tables 4 and 14) indicate, however, that only a small part of the arsenic in the parent rocks is retained in defluorinated phosphates.

TABLE 14.—*Arsenic in calcined, sintered, nodulized, and defluorinated phosphate rocks*

Unheated phosphate rock				Heated phosphate rock						Ratio of As in heated rock to As in unheated rock [2]
Sample No.	Type or source	P_2O_5	As	Sample No.	Type of product	Maximal temperature [1]	Time of heating at maximal temperature [1]	P_2O_5	As	
		Per-cent	P. p. m.			°C.	Min-utes	Per-cent	P. p. m.	
1851	Florida land pebble___	34.88	8.4	1850	Calcined rock [3]_____	845	20	35.75	6.5	0.75
1853	_____do_____	30.37	10.5	1852	_____do [3]_____	870	20	35.29	5.2	.43
1855	_____do_____	34.41	7.6	1854	_____do [3]_____	900	5	35.29	11.7	1.5
1857	_____do_____	32.35	15.4	1856	_____do [3]_____	1,095	5	34.51	12.2	.74
1859	_____do_____	35.38	3.6	1858	_____do [3]_____	1,230	5	36.25	5.1	1.4
[4] 1918	Tennessee brown rock_	22.95	7.4	1917	Nodulized matrix [5]___	900	15	25.15	1.4	.17
1861	_____do_____	34.40	6.6	1860	Calcined rock [3]_____	980	([6])	35.28	6.3	.93
1863	_____do_____	34.52	11.9	1862	_____do [5]_____	1,150	([6])	34.98	6.7	.56
1924	_____do_____	32.94	7.2	1923	Nodulized sand [7]____	1,455	15	33.45	3.7	.51
[8] 1922	_____do_____	22.85	56.1	1921	Nodulized matrix [5]__	([6])	15	23.38	16.0	.28
[8] 1922	_____do_____	22.85	56.1	1919	Sintered matrix [9]____	([6])	([6])	23.79	8.2	.14
1865	Idaho, Conda_____	32.54	9.8	1864	Calcined rock [5]_____	910	45	34.41	9.5	.92
[10] 1447	Florida land pebble___	34.37	11.4	1492	Defluorinated rock [11]	1,400	40	37.24	<.1	<.01
([12])	Tennessee brown rock_	_____	_____	1478	_____do [13]_____	1,400	([6])	37.25	1.4	_____
([12])	_____do_____	_____	_____	1476	_____do [14]_____	1,600	([6])	28.95	<.1	_____
[10] 1252	Montana, Garrison____	36.92	41.0	1496	_____do [11]_____	1,400	40	38.85	5.4	.13

[1] Approximate.
[2] Calculated from the arsenic-phosphorus ratios of the heated rock and the unheated rock, respectively.
[3] Heated with fuel oil.
[4] Matrix.
[5] Heated with coal.
[6] Not known.
[7] The fuel consisted of a mixture of approximately 50 percent of carbon monoxide from a phosphorus-condenser operation and 50 percent of gas oil.
[8] Mixture of matrix and washed phosphate sand.
[9] Heated with coke.
[10] 40- to 80-mesh particles screened from crushed rock.
[11] Prepared in the laboratory by heating the phosphate rock in an electric furnace in the presence of water vapor (*99*).
[12] A sample of the phosphate rock was not available.
[13] Prepared on a semiworks scale by heating phosphate rock in an oil-fired rotary kiln in the presence of water vapor.
[14] Prepared by subjecting molten phosphate rock to the action of water vapor (*25*).

ARSENIC IN SUPERPHOSPHATES AND PHOSPHORIC ACID

Aside from its presence in the phosphate rock, arsenic may be introduced into superphosphate and phosphoric acid as an impurity in the sulfuric acid used to decompose the rock or in other reagents or fuels used in some of the manufacturing processes. The earlier investigators (5, 28, 58, 130, 131) attributed the arsenic in superphosphate principally, if not entirely, to its presence in the sulfuric acid. Sulfuric acid manufactured from pyrite or produced as a byproduct of the smelting of other sulfide ores is used extensively in the fertilizer industry; such acid, especially that made from pyrite, often contains considerable arsenic (1, 16, 28, 58, 88, 127, 130, 149, pp. 337–338).

Native sulfur is also an important source of sulfuric acid for the domestic fertilizer industry, but, unlike pyrite, it usually contains little or no arsenic. In 1859, Davy (28) remarked that sulfuric acid made from pyrite contains considerable arsenic, whereas native sulfur contains little or no arsenic and the sulfuric acid made therefrom is not so likely to contain this element. Davis and Davis (27) found no trace of arsenic in sulfur from the Texas deposits that were being worked in 1920, whereas a later sample of Texas sulfur, analyzed by Abel (2a), contained 7.0 p. p. m. of arsenic; the authors' analysis of a recent sample from Louisiana showed only 2.1 p. p. m. of arsenic. Phipson (108) reported that a sample of Sicilian sulfur was "quite exempt" from arsenic, and that only a trace of arsenic was present in volcanic sulfur of Hecla. According to Gibbs and James (47), two samples of Japanese sulfur contained 143 and 200 p. p. m. of arsenic, respectively, whereas the arsenic content of four samples of French sulfur did not exceed 33.3 p. p. m. In harmony with the usually low arsenic content of native sulfur, Wyld (149, p. 337) states:

Arsenic is rarely found, and never in more than insignificant traces, in acid which has been made from brimstone; most of the latter material, indeed, is used where acid free from arsenic is wanted.

The phosphoric acid required for the manufacture of double superphosphate [13] is made either by the sulfuric acid process (90, 144) or by smelting mixtures of phosphate rock, silica, and coke in electric or blast furnaces (17, 23, 37). The presence of arsenic in phosphoric acid produced by the sulfuric acid process, and in phosphate chemicals made therefrom has long been recognized (15, 39, 40, 88, 109, 120). Results, reported by Hill, Marshall, and Jacob (67), for arsenic in crude phosphoric acid manufactured commercially with sulfuric acid produced as a byproduct of copper-smelting operations in Tennessee and Montana are given in table 15. The Montana sulfuric acid is used extensively in the production of phosphoric acid for the manufacture of double superphosphate, and large tonnages of superphosphates are made with the Tennessee sulfuric acid.

[13] The term "double superphosphate" refers to the fertilizer material, usually containing about 45 to 50 percent of P_2O_5, made by treating phosphate rock with phosphoric acid. The term is synonymous with the terms "triple superphosphate" and "treble superphosphate."

TABLE 15.—*Arsenic in crude phosphoric acid manufactured by the sulfuric acid process*

Type or source of phosphate rock	Source of sulfuric acid	Arsenic content of phosphoric acid [1]	
		Dilute [2]	Concentrated [3]
		P. p. m.	*P. p. m.*
Florida land pebble_____	Copper-smelting operation in Tennessee [4] _____	35.9	19.3
Tennessee brown rock____	____do [4]_____	50.7	30.5
Idaho_____	Copper-smelting operation in Montana [5] _____	840.0	1,161.6

[1] Data reported by Hill, Marshall, and Jacob (*67*); results calculated to basis of acid containing 50 percent of H_3PO_4.
[2] The dilute acids made from the Florida, Tennessee, and Idaho phosphate rocks contained 27.42, 22.12, and 27.96 percent of H_3PO_4, respectively.
[3] The concentrated acids made from the Florida, Tennessee, and Idaho phosphate rocks contained 60.93, 57.11, and 52.19 percent of H_3PO_4, respectively.
[4] A sample of acid (60° B.) from this smelting operation contained 11.4 p. p. m. of As.
[5] A sample of acid (50° B.) from this smelting operation contained 841 p. p. m. of As.

Isakov (*78*) expressed the opinion, unsupported by experimental data, that the arsenic in thermal phosphoric acid comes from the phosphate ore and coke used in the process. As pointed out in a preceding paragraph, arsenic is a common constituent of coal and coke. In view of the volatility of arsenic compounds at high temperatures, phosphoric acid produced by furnace methods would be expected to be contaminated with arsenic from the coke used in the process. Swann (*132*) and Carothers (*17*) state that precipitator acid (85 to 95 percent H_3PO_4) made by direct combustion of the electric-furnace gases contains about 100 to 150 p. p. m. of arsenic. According to information supplied to the authors by several domestic manufacturers, crude elemental phosphorus made from Florida land-pebble and Tennessee brown-rock phosphates by the electric-furnace process contains approximately 60 to 75 p. p. m. of arsenic, whereas the crude acid (about 75 to 80 percent H_3PO_4) made from this phosphorus contains approximately 19 to 45 p. p. m. Crude elemental phosphorus made by the blast-furnace process contains approximately 120 to 150 p. p. m. of arsenic, or about twice the arsenic content of phosphorus made by the electric-furnace process.

The foregoing figures are very much smaller than those (0.53 to 1.92 percent) reported by Hampe (*57*), Husemann (*76*), and Winkler (*147*) for arsenic in elemental phosphorus produced in Europe during the last quarter of the nineteenth century. At that time, however, elemental phosphorus was commonly manufactured by distilling a mixture of coke and sirupy phosphoric acid (*113*); the acid was made by treating bone ash or phosphate rock with sulfuric acid and concentrating the dilute product. Thus the arsenic in the elemental phosphorus may have been derived from three sources, namely, the phosphatic raw material, the sulfuric acid (made principally, if not entirely, from pyrite), and the coke, of which the sulfuric acid probably contributed by far the greater portion.

Angell and Angell (*5*), Haselhoff (*58*), Stoklasa (*130*), and Stutzer (*131*) reported 40 to 2,600 p. p. m. of arsenic in samples of European ordinary superphosphates [14] manufactured about 40 years ago, princi-

[14] The term "ordinary superphosphate" refers to the fertilizer material, usually containing about 16 to 20 percent of P_2O_5 and consisting of a mixture of approximately equal parts by weight of monocalcium phosphate and calcium sulfate, made by treating phosphate rock with sulfuric acid.

pally, if not entirely, with sulfuric acid produced from pyrite. On the other hand, Headden (59) found only about 1 p. p. m. of arsenic in a sample of American ordinary superphosphate, the only analysis of such material that has come to the authors' attention. The authors' results (table 16) for arsenic in ordinary superphosphate made with sulfuric acid produced entirely or partially from pyrite range from 494.1 to 1,199.1 p. p. m. and are very much higher than those (2.2 to 35.7 p. p. m.) for superphosphate made with acid produced entirely from native sulfur or as a byproduct of smelting operations or recovered from the raffination of petroleum. Aside from the superphosphates made with acid produced entirely or partially from pyrite, the weight ratio of arsenic in a given quantity of the superphosphate to arsenic in the corresponding quantity of the phosphate rock (table 16, column 9) is usually less than 2, thereby indicating that the phosphate rock is the principal source of arsenic in most of the samples.

Analyses reported by Young (151) and by the manufacturer [15] show 1,000 p. p. m. and 908.8 p. p. m. of arsenic, respectively, in samples of double superphosphate made from Idaho phosphate rock with phosphoric acid produced with sulfuric acid manufactured from Montana sulfide ores; the authors' result on a sample of double superphosphate from this source is 404.6 p. p. m. of arsenic (No. 1372, table 16). The results on samples of double superphosphate made from Florida land-pebble, Tennessee brown-rock, and Montana phosphates with phosphoric acid produced with sulfuric acid manufactured from elemental sulfur or as a byproduct of copper- and zinc-smelting operations in Tennessee and British Columbia, respectively, range from 10.6 to 64.9 p. p. m.; the data (see tables 8 and 16), like those for ordinary superphosphates made with sulfuric acid from the same sources, indicate that the phosphate rock was the principal source of arsenic in these samples.

TABLE 16.—*Arsenic in superphosphates*

ORDINARY SUPERPHOSPHATES

Phosphate rock [1]				Source of sulfuric acid	Superphosphate [1]			Ratio of As in superphosphate to As in phosphate rock [2]
Sample No.	Type or source	P_2O_5	As		Sample No.	P_2O_5	As	
		Per-cent	P. p. m.			Per-cent	P. p. m.	
1875	Florida land pebble	33.30	9.8	Louisiana sulfur [3]	1874	20.48	5.2	0.86
1893	do	32.56	8.7	Texas sulfur	1892	20.48	10.1	1.8
1879	do	32.10	16.2	do	1877	21.00	7.2	.68
1867	do	35.21	4.3	Domestic sulfur	1866	21.85	4.1	1.5
1889	Tennessee brown rock	33.24	6.4	do	1888	19.83	4.5	1.2
1899	do	34.64	6.5	Texas sulfur	1898	21.55	14.3	3.5
1884	Florida land pebble	33.86	15.2	Louisiana sulfur and Spanish pyrite.[4]	1883	20.93	1,096.6	116.7
1882	do	33.16	8.2	Domestic sulfur and Spanish pyrite.[5]	1881	21.00	1,199.1	230.9
1891	do	33.53	8.4	Spanish pyrite [6]	1890	20.83	494.1	94.7
1895	do	32.78	12.4	Copper-smelting operation in Tennessee.[7]	1894	20.43	8.3	1.1
1873	do	33.76	12.0	do [7]	1872	20.78	6.0	.81

See footnotes at end of table.

TABLE 16.—*Arsenic in superphosphates*—Continued

ORDINARY SUPERPHOSPHATES—Continued

Phosphate rock [1]				Source of sulfuric acid	Superphosphate [1]			Ratio of As in superphosphate to As in phosphate rock [2]
Sample No.	Type or source	P_2O_5	As		Sample No.	P_2O_5	As	
		Per-cent	P. p. m.			Per-cent	P. p. m.	
1871	Tennessee brown rock	34.37	5.0	Copper-smelting operation in Tennessee.[7]	1870	20.30	9.2	3.1
1897	...do...	34.73	7.7	...do[7]	1896	21.43	11.3	2.4
1869	...do...	34.60	13.0	Zinc-smelting operation in Illinois.[6]	1868	21.20	2.2	.28
1930	Montana, Garrison	31.51	58.4	Zinc-smelting operation in British Columbia.[9]	1928	20.00	35.7	.96
(10)	Florida land pebble			[11]	1403	20.56	9.8	
(10)	...do...			[12]	1402	20.60	30.6	
(10)	Idaho, Conda			Not known	1933	20.33	9.8	
(10)	...do...			...do	1887	21.45	14.6	

DOUBLE SUPERPHOSPHATES

1879	Florida land pebble	32.10	16.2	Texas sulfur	1878	48.84	11.6	.47
(10)	...do...			Domestic sulfur	1880	49.53	10.6	
(10)	Tennessee brown rock			Copper-smelting operation in Tennessee.[7]	1481	44.08	34.3	
(10)	...do...			...do[7]	1900	47.01	20.8	
1930	Montana, Garrison	31.51	58.4	Zinc-smelting operation in British Columbia.[9]	[13]1929	45.65	64.9	.77
(10)	Idaho, Couda			Iron sulfide concentrate [14]	1372	47.33	404.6	
(10)	Tennessee brown rock			[15]	1362	48.37	118.5	
(10)	...do...			[15]	1950	50.31	100.1	
(10)	...do...			[16]	1886	47.48	22.9	
1926	...do...	31.81	13.3	[17]	1925	50.69	11.1	.52
(10)	Florida land pebble			[18]	1945	50.63	14.3	

[1] The analyses are not converted to the moisture-free basis.
[2] Calculated from the arsenic-phosphorus ratios of the superphosphate and the phosphate rock, respectively.
[3] A sample of the sulfur contained 2.1 p. p. m. of As.
[4] Approximately one-third of the acid was made from sulfur and two-thirds from pyrite.
[5] One-fourth of the acid was made from sulfur and three-fourths from pyrite.
[6] According to the manufacturer, the acid (55° B.) contained 910 p. p. m. of As.
[7] A sample of acid (60° B.) from this smelting operation contained 11.4 p. p. m. of As (67).
[8] According to the manufacturer, the acid from this smelting operation usually contains less than 5 p. p. m. of As.
[9] According to the manufacturer, the acid (98 percent H_2SO_4) from this smelting operation contains less than 0.1 p. p. m. of As.
[10] A sample of the phosphate rock was not available.
[11] The acid was processed sludge acid from the raffination of asphalt-base petroleum.
[12] The acid was untreated sludge acid from the raffination of asphalt-base petroleum.
[13] Ammoniated double superphosphate, made with synthetic ammonia.
[14] Obtained by floating the tailings from a copper-ore concentrator in Montana.
[15] The phosphoric acid was made by the blast-furnace process.
[16] The phosphoric acid was made by the electric-furnace process with direct oxidation of the furnace gas.
[17] The phosphoric acid was made by the electric-furnace process; about one-third of the acid was made by direct oxidation of the phosphorus.
[18] The phosphoric acid was made by the electric-furnace process with condensation and subsequent oxidation of the phosphorus.

The high contents of arsenic (118.5 and 100.1 p. p. m.) in the two samples of double superphosphate (Nos. 1362 and 1950, table 16) made with phosphoric acid produced by the blast-furnace process indicate contamination with arsenic present as an impurity in the coke used in the process. On the other hand, the arsenic (11.1 to 22.9 p. p. m.) in the samples of double superphosphate (Nos. 1886, 1925, and 1945) made with electric-furnace phosphoric acid seems to have come principally, if not entirely, from the phosphate rock.

Rader and Hill (*111*) have pointed out that superphosphates, because of the presence of active fluorine compounds, readily attack glass and cannot be stored in glass bottles without danger of becoming contaminated with boron from the container. Contamination of superphosphates and phosphoric acid with arsenic may also occur in the same way. For example, analyses of a sample of fresh ordinary superphosphate that had remained undisturbed in a glass bottle for about a year showed 12.9 p. p. m. of arsenic in the material in contact with the walls of the bottle whereas, the material from the center of the bottle contained only 3.7 p. p. m. On the other hand, two samples of cured double superphosphate (Nos. 1362 and 1372, table 16) showed the same arsenic contents in portions stored for several years in wooden or fiberboard containers and in glass bottles, respectively. In order to avoid this possible source of contamination, all the analyses reported in table 16 were made on superphosphates that had never been stored in glass.

ARSENIC IN AMMONIUM PHOSPHATE, BONE, AND MISCELLANEOUS PHOSPHATE FERTILIZERS

The results for arsenic in three samples of fertilizer-grade ammonium phosphate made from Florida land pebble with sulfuric acid produced from elemental sulfur (table 17) fall within the range for arsenic in this type of phosphate rock (table 3). Likewise, the arsenic content of the ammonium phosphate (No. 1885) made from Garrison, Mont., rock with byproduct sulfuric acid is within the range of results (table 6) on phosphate rock from this locality. It appears, therefore, that the phosphate rock was the principal source of arsenic in the products. These figures are very much lower than that (1,200 p. p. m.) obtained by Young (*151*) on a sample of ammonium phosphate made from Idaho rock with sulfuric acid produced from Montana sulfide ores. Although other results for arsenic in ammonium phosphates have not come to the authors' attention, it is interesting to note that Longfield-Smith (*94*) found 189 to 1,136 p. p. m. in five samples of Nitrophoska [16] imported from Germany.

The authors' results for arsenic in imported and domestic basic slags (table 17) are far lower than that (12,118 p. p. m.) reported by Kryukov (*89*) for a sample produced in the Union of Soviet Socialist Republics. Likewise, the figure for arsenic in the sample of crude dicalcium phosphate is only a small fraction of those (280 to 1,700 p. p. m.) reported by Fresenius (*40*) for precipitated phosphate made in Europe about 50 years ago.

Arsenic, ranging in quantity from 0.2 to 2.2 p. p. m., was present in five samples of bonemeal and bone ash, and a sample of Peruvian guano contained 24.9 p. p. m. (table 17). Longfield-Smith (*94*) reported a trace of arsenic in a sample of raw bonemeal and 189 p. p. m. of arsenic in a guano from an unstated source. The arsenic content of the samples of fossil teeth and bone (table 17) is more than double that of the samples of modern bone but is no greater than the arsenic content of some samples of Florida phosphate rock (table 3).

[16] Nitrophoska is the trade name of a series of high-analysis fertilizer mixtures of German manufacture (*122, p. 442*). All members of the series contain diammonium phosphate. The other components of the mixtures are ammonium nitrate or urea and potassium chloride or potassium sulfate.

Small quantities of arsenic were present in samples of calcium metaphosphate, Non-Acid phosphate, and flue dust from a phosphoric acid blast-furnace (table 17).

TABLE 17.—*Arsenic in ammonium phosphate, bone, and miscellaneous phosphate fertilizers*

Sample No.	Material	P_2O_5[1]	As[1]
		Percent	*P. p. m.*
1885	Ammonium phosphate [2]	48. 99	74. 2
1849	----do [3]	49. 37	15. 1
1901	----do	50. 49	17. 1
1902	----do [4]	22. 80	5. 5
974	Basic slag, domestic	8. 66	11. 2
1164	Basic slag, imported	18. 45	6. 2
1108	----do	19. 07	2. 1
971	Bone ash	40. 36	[5] ≤.8
780	Bonemeal	21. 62	2. 2
778	----do	31. 63	. 2
777	----do	33. 11	1. 1
1165	----do	34. 56	. 6
1755	Fossil bone [6]	36. 90	5. 0
1754	Fossil teeth [6]	37. 67	4. 5
1475	Calcium metaphosphate [7]	63. 87	2. 6
1021	Dicalcium phosphate [8]	40. 20	7. 4
1588	Flue dust from phosphoric acid blast-furnace [9]	52. 31	3. 2
1106	Guano, Peruvian	14. 40	24. 9
1172	Non-acid phosphate [10]	26. 56	3. 1

[1] The analyses are not converted to the moisture-free basis.
[2] Monoammonium phosphate, fertilizer-grade, made from phosphoric acid produced from Garrison, Mont., phosphate rock by the sulfuric acid process. The sulfuric acid, manufactured in British Columbia from zinc-smelter gases, is said to contain less than 0.1 p. p. m. of As on the basis of 98 percent H_2SO_4.
[3] Monoammonium phosphate, fertilizer grade, made from phosphoric acid produced from Florida land-pebble phosphate by the sulfuric acid process. The sulfuric acid was made from domestic sulfur.
[4] Mixture of monoammonium phosphate and ammonium sulphate, fertilizer-grade. The phosphoric acid was made from Florida land-pebble phosphate by the sulfuric acid process. The sulfuric acid was made from domestic sulfur.
[5] Analysis reported by Jacob, Hill, Marshall, and Reynolds (*81, p. 30*).
[6] From Florida land-pebble phosphate deposit.
[7] Made by reacting phosphorus pentoxide with Tennessee brown-rock phosphate (*24*).
[8] Crude material made from phosphoric acid produced from Florida land-pebble phosphate by hydrochloric acid treatment. The hydrochloric acid was obtained as a byproduct of the manufacture of salt cake.
[9] Tennessee brown-rock phosphate was smelted in this furnace. The flue dust also contains considerable potassium (*136*).
[10] Manufactured in 1925 by heating Florida land-pebble phosphate with a potassium salt (*2*).

Although no determinations of arsenic in nitrogenous and potassic fertilizers were made by the authors, results obtained by other workers are of interest. Thus, Longfield-Smith (*94*) found traces of arsenic in samples of tankage, castor pomace, cottonseed meal, kainite, potassium nitrate, potassium sulfate, and Chilean sodium nitrate; a sample of synthetic sodium nitrate contained 235 p. p. m. of arsenic, and 24 samples of ammonium sulfate contained 0 to 1,666 p. p. m. (average 682 p. p. m.). Abel (*2a*) reported 3.1 to 1,098.1 p. p. m. of arsenic in five samples of ammonium sulfate and 3.4 p. p. m. in a sample of iron sulfate. By use of a spectrochemical method, Gaddum and Rogers (*42*) found arsenic, ranging in quantity between 1,000 and 5,000 p. p. m., in a sample of ammonium sulfate, but they were unable to detect arsenic in other samples of a wide variety of fertilizer and liming materials, elemental sulfur, and sulfates of barium, cadmium, cobalt, copper, iron, magnesium, manganese, nickel, and zinc. The spectrochemical analyses of Noddack and Noddack (*104*) showed no arsenic in Stassfurt carnallite, 1 p. p. m. in Stassfurt kainite, and 0.2 p. p. m. in Chilean sodium nitrate.

EFFECT OF ARSENIC ON PLANTS AND SOIL ORGANISMS

In view of the general presence of arsenic in phosphates, the question of the effects of this element on plants and on the soil population naturally arises. Although the authors have done no work in this field, numerous investigations have been made by others. The following summaries of some of the results afford a basis for the evaluation of the probable effects of the quantities of arsenic present in phosphate fertilizers.

In 1859, Davy (*28*) reported that transplanted pea plants suffered no pronounced injurious effects when they were watered with a saturated solution of arsenious oxide at 2- to 3-day intervals for more than a week. Stewart and Smith (*129*) stated that growth of beans and potatoes in plots of gravelly bench loam seemed to be stimulated by the presence of 25 p. p. m. of arsenic added as disodium arsenate 3 to 6 weeks after the appearance of the plants above the soil; peas and wheat seemed to be stimulated by arsenic in concentrations as high as 75 p. p. m., and radishes by concentrations as high as 250 p. p. m. In each case, higher concentrations of arsenic were toxic, roughly in proportion to the quantity applied. In pot experiments with barley, Vandecaveye, Horner, and Keaton (*140*) found that addition of 39 p. p. m. of arsenic as arsenious oxide to a fertile soil that had never been subjected to arsenical sprays caused only very slight symptoms of arsenic poisoning in the seedlings. The toxic effect increased with larger quantities of arsenic, and with 136 p. p. m. the plants failed to survive the shooting stage. With soils from orchards that had been sprayed with lead arsenate, the crops of alfalfa and barley were good when the content of water-soluble arsenic was 1.5 p. p. m. or less, and very poor when it was 3 to 12 p. p. m.

Young (*151*) reported a stimulating effect on growth of timothy from arsenic (0.1 to 10 p. p. m.) added to tumblers of adequately fertilized Merrimac coarse sandy loam, whereas arsenic was highly toxic in concentrations of 100 p. p. m. or more. A low concentration of arsenic (2 p. p. m.) stimulated the growth of green algae (*Crucigina* and an organism designated as No. 4) in culture media, but higher concentrations (20 p. p. m. or more) were toxic.

Morris and Swingle (*102*) studied the effect of numerous arsenic compounds on a wide variety of plants under greenhouse conditions. Transpiration of tomato plants was decreased by 7.5 p. p. m. of arsenic as arsenious oxide, and the injury increased in direct proportion to the concentration of arsenic; similar results were obtained with sodium and potassium arsenites. Beans and cucumbers were very susceptible to arsenic, but the cereals and grasses were much more resistant. Confirming the earlier observations of Stoklasa (*130*), the arsenites were decidedly more toxic than the arsenates. Furthermore, the compounds differed considerably in their reaction in the soil, some becoming inert in a much shorter time than others. According to Abel (*2a*), injury to pineapple plants has been reported in Hawaiian areas where the plants were fertilized with an ammonium sulfate that contained 1098.1 p. p. m. of arsenic. This injury is believed to have been caused by the arsenic in the fertilizer.

Experiments by Dorman, Tucker, and Coleman (*34*), with several important soil types of the Cotton Belt, showed no germination- or

seedling-injury to oats, Austrian Winter peas, and hairy vetch from the application of 400 pounds of calcium arsenate per acre, equivalent to approximately 75 p. p. m. of arsenic, immediately before planting. Although larger applications were injurious and the effect was more serious on the lighter soils, much of the toxicity of the arsenate was lost in the first year.

Stoklasa (130) observed that growth of oats in sand culture was stimulated by addition of 15 p. p. m. of arsenic (as arsenic pentoxide) to the phosphorus-free nutrient solution, whereas the arsenic had no stimulating effect in the presence of an adequate supply of phosphorus. Hurd-Karrer (75) obtained indications that phosphate applications reduce or prevent arsenic injury to plants where the type of soil is such as to permit the phosphate to remain available.

The effect of arsenic on the ammonifying, nitrifying, and nitrogen-fixing organisms of the soil has been studied by Greaves (51). With lead arsenate, an application of 60 p. p. m. of arsenic markedly stimulated nitrification, and 350 p. p. m. was not harmful. Ammonification was reduced about 50 percent by 1,250 p. p. m. of arsenic, whereas fixation of atmospheric nitrogen was doubled by 250 p. p. m. Paris green was much more toxic to the organisms than was lead arsenate.

Stewart and Smith (129) found that absorption of arsenic by plants increased with the quantity applied to the soil and reached values as high as 2,150 p. p. m. in pea plants (dry basis) grown on soil to which 500 p. p. m. of arsenic had been added. Vandecaveye and coworkers (140) reported 13.3 p. p. m. of arsenic in the tops of barley grown on arsenic-contaminated soil, whereas the roots contained 1,250 p. p. m. Arsenic was present in the leaf blades and petioles of rhubarb, in the young leaves of rye and buckwheat, and in the stems, leaves, and green pods of broadbeans grown by Angell and Angell (5) on soil fertilized with superphosphate in which the arsenic content had been increased to 3,800 p. p. m. by addition of arsenious oxide, but no trace of arsenic was found in the fruit or seed of any of the plants. Analyses by Williams and Whetstone (146) showed 0 to 10 p. p. m. of arsenic (average less than 0.77 p. p. m.) in the air-dry substance of 91 samples of numerous species of cultivated and wild plants from various sections of the United States, grown on soils containing 4 to 36 p. p. m. of arsenic (average 8 p. p. m.) on the air-dry basis. According to Grimmett and coworkers (52, 54) samples of oat straw and grain grown on natural arsenical soils in New Zealand contained only 3.0 and 2.3 p. p. m. of arsenic, respectively, and were not harmful to stock. Likewise, pasture grasses grown on these soils and containing 0.5 to 17.4 p. p. m. of arsenic were not toxic to animals grazed thereon.

ARSENIC SUPPLIED TO SOIL BY SUPERPHOSPHATE

The annual application of phosphate fertilizer to the soils of the United States seldom, if ever, exceeds the equivalent of 2,000 pounds of ordinary superphosphate per acre; in general farming, the application is seldom equivalent to more than 200 pounds of superphosphate per acre; usually it is much less. Now let it be supposed that a superphosphate containing approximately 1,200 p. p. m. of arsenic, the largest quantity found in any material analyzed in this investigation (No. 1881, table 16), is applied to the soil at the rate of 2,000 pounds per acre within 3 inches of the plant rows, which are 3 feet apart.

Then assuming the customary figure, 2,000,000 pounds of soil in the plowed layer (6⅔ inches) of an acre, the increase in the arsenic concentration of the entire layer would be 1.2 p. p. m., and the increase in the concentration in the layer extending 3 inches on either side of the row, if all the arsenic were retained therein, would be 7.2 p. p. m. With a 200-pound application of this superphosphate the increases in arsenic concentration would be 0.12 and 0.72 p. p. m., respectively. Analyses of 30 samples of ordinary and double superphosphates, typical of these materials as used in all sections of the United States, gave an average of 126.2 p. p. m. of arsenic (table 16). With a 2,000-pound application of superphosphate containing this quantity of arsenic the respective increases in the concentrations of arsenic in the soil would be 0.126 and 0.756 p. p. m., whereas with a 200-pound application the increases would be only 0.0126 and 0.0756 p. p. m., respectively.

When all the factors affecting the action of arsenic on plants and on soil organisms under practical conditions of farming are taken into consideration, it seems highly improbable that the arsenic in domestic phosphate fertilizer exerts any toxic effects, even with very large annual applications of the fertilizer over extended periods of time. Likewise, Haselhoff (58) concluded that the arsenic content of European superphosphates (40 to 1,490 p. p. m.) was not sufficient to have an injurious effect on plants under practical conditions. According to Stoklasa (130), superphosphate is not dangerous to vegetation unless it contains more than 4,000 p. p. m. of arsenic, and Stutzer (131) expressed the opinion that the arsenic content of superphosphate(100 to 500 p. p. m.) is too low to render plants fertilized therewith poisonous to animals. Headden (59) states:

There is no question but that soils which may have originally been entirely free from arsenic might show its presence after years of fertilization with superphosphate, but the accumulation in this manner is extremely slow compared with its rate of increase in cases where spraying [of orchards or crops with arsenic compounds] is practiced.

SUMMARY AND CONCLUSIONS

Results are given for acid-soluble arsenic in 210 samples of mineral phosphates from various deposits of the world; 16 samples of calcined, sintered, nodulized, and defluorinated phosphates of domestic origin; 30 samples of commercial ordinary and double superphosphates manufactured from domestic rock; 6 samples of crude phosphoric acid produced by the sulfuric acid process; and 19 samples of ammonium phosphate, basic slag, bone materials, and miscellaneous phosphate fertilizers.

It is shown that arsenic occurs in phosphate rock principally, if not entirely, in the acid-soluble condition, and that the presence of fluorine compounds causes serious error in its determination unless arsenic-free glassware is used for the acid digestion. The danger of contamination of samples of fluorine-bearing phosphoric acid and superphosphate with arsenic from glass containers is pointed out.

The results for arsenic in mineral phosphates range from 0.4 p. p. m. in a Florida soft phosphate to 188.2 p. p. m. in an Arkansas phosphate. With the different types and sources of domestic phosphate the average results (p. p. m.) are in the descending order, South Carolina river rock 68.4, Arkansas 61.0, Montana 47.6, Tennessee blue rock 20.4,

Utah 17.8, Oklahoma 17.6, South Carolina land rock 17.1, Tennessee brown rock and phosphatic limestone 14.6, Idaho 12.6, Wyoming 12.1, Florida land pebble 11.9, Tennessee white rock 10.6, Kentucky 9.9, Florida waste pond 9.0, Florida soft 7.5, Virginia fluorapatite 5.5, and Florida hard rock 5.4.   The results for foreign phosphates range from 5.1 p. p. m. in a calcium phosphate from Nauru Islands to 76.2 p. p. m. in an aluminum iron phosphate from Daito Islands.

The occurrence of arsenic in mineral phosphates is discussed from the following points of view: (1) Arsenic-bearing constituents; (2) primary and secondary deposits; (3) geologic age of deposits; and (4) a comparison of phosphates with other rocks, minerals, coals, soils, sediments, and waters.   Accordingly, the data indicate that there is, in general, no orderly relationship between the arsenic content and the geologic age of phosphate rock or between the arsenic content and the quantities of other constituents (phosphorus, iron, sulfide sulfur, organic carbon, or nitrogen), although the arsenic follows the inorganic sulfides and organic matter in the mechanical fractions of certain phosphates (Cokeville, Wyo., and Conda, Idaho).   There is evidence that phosphates from primary deposits tend to contain somewhat more arsenic than do those from secondary deposits.   The arsenic content of mineral phosphates is similar, in general, to that of marls, domestic shales, carbonate minerals, coals, and silicate rocks and minerals; usually it is higher than that of soils, clays, sediments, and nitrate and halide minerals, but is much lower than that of oxide minerals, greensand, glauconite, and especially sulfide minerals.

In proportion to their phosphorus contents, calcined, sintered, or nodulized phosphates usually contain notably less arsenic than do the parent phosphate rocks.   Only a small portion of the arsenic in the parent phosphate rock is retained in defluorinated phosphate.

The results for arsenic in ordinary superphosphates made with sulfuric acid produced entirely or partially from pyrite range from 494.1 to 1,199.1 p. p. m. and are very much higher than those (2.2 to 35.7 p. p. m.) for superphosphate made with acid produced entirely from native sulfur or as a byproduct of certain smelting operations in Illinois and Tennessee.   Except for material made with acid produced entirely or partially from pyrite, the phosphate rock is the principal source of arsenic in most superphosphates.

The results for arsenic in double superphosphates range from 10.6 p. p. m. in a material made with phosphoric acid produced with sulfuric acid manufactured from native sulfur to 404.6 p. p. m. in a material made with the aid of sulfuric acid produced from Montana sulfide ores.   Owing to contamination of the product with arsenic from the fuel (coke), the arsenic content (100.1 to 118.5 p. p. m.) of double superphosphate made with blast-furnace phosphoric acid is much higher than that (11.1 to 22.9 p. p. m.) of double superphosphate made with electric-furnace acid.

Arsenic was found in ammonium phosphate (5.5 to 74.2 p. p. m.), basic slag (2.1 to 11.2 p. p. m.), and bone ash and bonemeal (0.2 to 2.2 p. p. m.).   Calcium metaphosphate, fossil bone and teeth, dicalcium phosphate, flue dust from a phosphoric acid blast-furnace, Non-Acid phosphate, and Peruvian guano contained arsenic in quantities ranging from 2.6 in the first material to 24.9 p. p. m. in the last.

When all the factors affecting the action of arsenic on plants and on soil organisms under practical conditions of farming are taken into consideration, it seems very unlikely that the quantities of arsenic contributed to the soil in phosphate fertilizers are sufficient to produce toxic effects even with very large annual applications of the fertilizer over extended periods of time.

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